

Influence of charge on the structures for small Si_n clusters

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Abstract:-We have investigated the influence of charge on the ground state structures for small Si_n ($n=5-10$) clusters by using the full-potential linear muffin-tin orbital molecular-dynamics (FP-LMTO-MD) method. Addition or removal of one or two electrons does not change the geometrical configurations of the small Si_n ($n=5-10$) clusters even though they undergo some structural distortion. But the structural distortion is different for the small Si cluster with different atomic number as charge increases. The distortion arises from the electrostatic repulsion among the charged atoms, and the change of bonding characteristic for some atoms.

Key-Words:- silicon cluster, stable structure, ion, distortion, molecular-dynamics simulation, charge

1 Introduction

Silicon clusters have attracted significant interest in recent years. Investigations of their electronic and geometric structures are of scientific importance. During the past decades, theoretical and experimental studies are focused on the small silicon clusters because larger clusters can fragment into the small clusters. Experimentally, the small silicon clusters with 4, 6, 7 and 10 atoms are much more stable than other clusters [1-3]. The structures of the small neutral silicon clusters have been accepted universally. Si_3 has a bent equilibrium geometry (C_{2v}). The ground state geometry of Si_4 is a rhombus with D_{2h} . The lowest energy structures of Si_{5-7} are a trigonal bipyramid (D_{3h}), a tetragonal bipyramid (D_{4h}) and a pentagonal bipyramid (D_{5h}), respectively. For Si_{8-10} , a C_{2h} distorted bicapped octahedron, a C_{2v} bicapped pentagonal bipyramid and a C_{3v} tetracapped trigonal prism have been regarded as their most stable structures [4]. We have also investigated the geometrical structures of the small Si_n clusters using full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) method [5-7]. Our calculated results are in good agreement with experimental values and theoretical results obtained by other methods.

Experimentally, more attention has focused on the ionic silicon clusters because of the high ionization energy of the Si_n clusters [8]. According to a collision-induced dissociation study, the cationic Si_n^+ clusters containing up to 60 atoms dissociate mainly by loss of Si_6 or Si_{10} species and little by the loss of Si_7 or

Si_{11} [9]. These are consistent with prominent presence of Si_6^+ , Si_7^+ , and Si_{10}^+ ions in the mass spectra [3,10].

Up to now, some theoretical calculations on the charged Si_{4-10} clusters have been also done [3,11]. Their ionic structures are similar to those of their corresponding neutral clusters. But, to the best of our knowledge, the investigations on the evolution of the small Si_n ($n=5-10$) clusters as a function of charging have not been reported. In fact, the studies are helpful for us to understand the physical and chemical properties of the Si_n clusters in detail.

In this paper, we have performed careful investigations on the change of geometrical structures for the small Si_n ($n=5-10$) clusters as a function of charging using full-potential linear-muffin-tin-orbital molecular-dynamics method. Our aim is to investigate the physical properties of the small Si cluster ions, and make comparative study with their corresponding neutral clusters. The results are presented in the third section and discussed.

2 Method

The FP-LMTO method is a self-consistent implementation of the Kohn-Sham equations in the local-density approximation [12-15]. During the molecular-dynamics calculations, space is divided into two parts: non-overlapping muffin-tin (MT) spheres centered at the nuclei, and the remaining interstitial region. LMTOs are augmented Hankel functions inside the MT spheres, but not in the interstitial region [15-18]. Self-consistent filed calculations are carried out with a

convergence criteria of 10^{-5} a.u. on the total energy and 10^{-3} a.u. on the force.

The method is suitable for investigating the geometrical structures of semiconductor [7,19]. The calculating results from the method are in good agreement with those obtained by some other advanced molecular dynamics methods [20]. In order to compare with those obtained by 6-31G* and MP4/6-31G* calculations [21] and the experimental values [22-28], our results for the small Si_{2-8} clusters are presented in Table 1. The calculated Si-Si bond lengths are expected to be reliable to within 1-2% [21]. In MP4/6-31G* calculations, comparison with the corresponding experimental values suggests that about 80-85 % of the true binding energy is obtained. A scale

factor of 1.2 empirically corrects for the under-estimations, and yields binding energies in good agreement with experiment [1]. Using the FP-LMTO-MD method, we have also obtained the same ground state structures for the Si_{2-8} clusters. The geometrical parameters are in consistent with those obtained by other LDF methods. We haven't listed the values repeatedly here. Although the calculated cohesive energies (binding energy per atom) are larger than the corresponding experimental values, we find that a scale factor of 0.77 empirically corrects for the overestimations, and yields binding energies in excellent agreement with experiment values. The use of such a single uniform scale factor does not bias the relative comparisons of the different clusters.

Cluster	Si_2	Si_3	Si_4	Si_5	Si_6	Si_7	Si_8
E_t (HF/6-31G*)	1.47	2.96	5.90	7.24	9.90	12.08	13.20
E_t (MP4/6-31G*)	2.60	6.34	10.57	13.74	18.02	22.16	24.31
E_t (FP-LMTO-MD)	4.05	9.97	15.81	21.30	26.97	32.61	36.34
E_c (HF/6-31G*)	1.30	2.11	2.64	2.75	3.00	3.17	3.04
E_c (FP-LMTO-MD)	2.02	3.32	3.95	4.26	4.50	4.66	4.54
E_s (MP4/6-31G*)	1.56	2.54	3.17	3.30	3.60	3.80	3.65
E_s (FP-LMTO-MD)	1.56	2.54	3.05	3.28	3.47	3.59	3.50
E_{exp}	1.66	2.44	2.99	3.24	3.43	3.53	3.54

Table 1: Calculated total binding energy (E_t , in eV), cohesive energy (E_c , in eV), scaled cohesive energy (E_s , in eV), and the measured cohesive energy (E_{exp} , in eV) by Knudsen mass spectrometers. The HF/6-31G* and MP4/6-31G* calculations are cited from Ref. [22]. The experimental results are quoted from Ref. [23-28].

3 Results and discussions

Fig1 shows the stable structures of Si_5 cluster and its ions. The bond lengths larger than 3.2\AA are not drawn in Fig.1. Neutral Si_5 cluster has a compact ground state structure. The bond lengths of d_{45} , d_{12} and d_{14} are 2.96\AA , 3.04\AA and 2.30\AA , respectively. Removal of one electron results in the increase of some bond lengths. But its geometrical configuration (not drawn in Fig.1) is similar. The ionic structure is not so compact as its neutral structure. Removal of more electrons makes its structure larger in space. In positive ion Si_5^{+2} , some bond strength becomes weaker. The distances between some atoms are larger than 3.5\AA . In fact, the ionic structure can be regarded as a tetragon with a surface atom. Its symmetry is C_{4v} . After four electrons are taken away, its symmetry becomes D_{3h} again. This structure suggests that the removed electrons are mainly from the side atoms. In addition, taking away more electrons results in unstable structure.

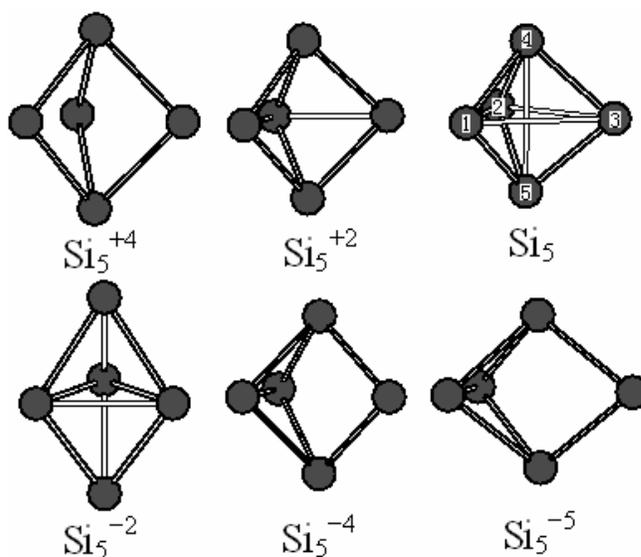


Figure 1 The stable structures of Si_5 cluster and its ions

On the contrary, addition of one or two electrons makes the bonds between side atoms 1, 2 and 3 stronger.

As a result, the bond between apex atoms 4 and 5 becomes weak. Further adding electrons result in more obvious structural distortion. It is found from observing two Si_5^{-4} and Si_5^{-5} ion structures that two atoms among three side atoms form a strong bond, at the same time, another side atom is repulsed. Obviously, the charge added does not distribute the atoms in the cluster uniformly.

The neutral and ionic geometrical structures of Si_6 cluster are shown as Figure 2. Si_6 cluster exhibits high stability compared with neighboring clusters. It is found from observing Fig.2 that charging on Si_6 cluster does not change its geometrical configuration except for local structural distortion. All the positive and negative ion structures are not so compact as its neutral structure. Most severe distortion occurs in Si_6^{-4} cluster ion.

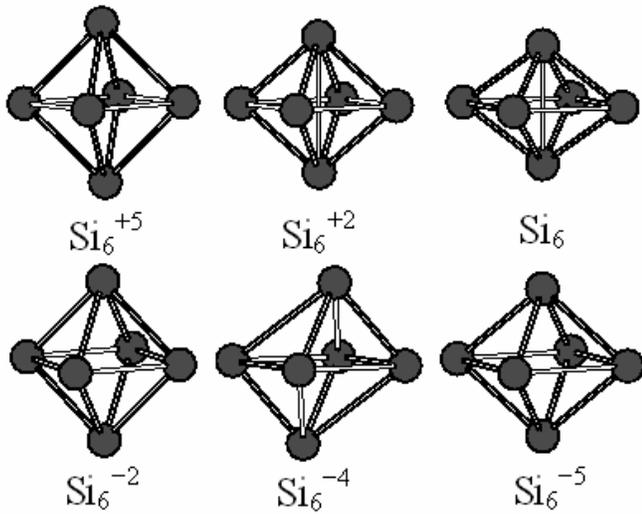


Figure 2 The stable structures of Si_6 cluster and its ions

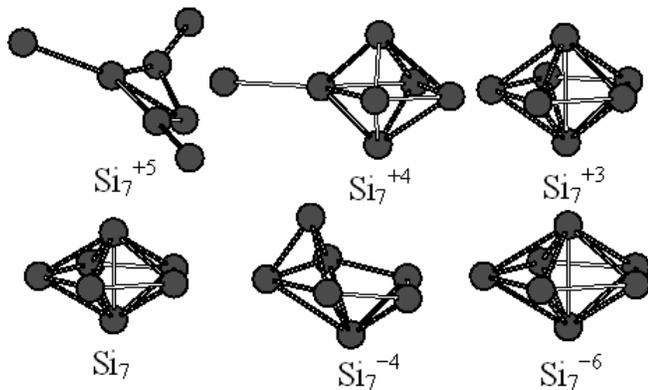


Figure 3 The stable structures of Si_7 cluster and its ions

For Si_7 cluster, the situation is somewhat different

(see Fig.3). When four electrons are taken away, it can be regarded as an adsorbed structure. One Si atom is adsorbed on an apex atom of Si_6 cluster. Removal of one more electron results in planar ionic structure. On the other hand, structural distortion also arises from addition of electrons. It is interesting that there is severe distortion in Si_7^{-4} cluster ion. But for Si_7^{-5} cluster ion, the distortion decreases.

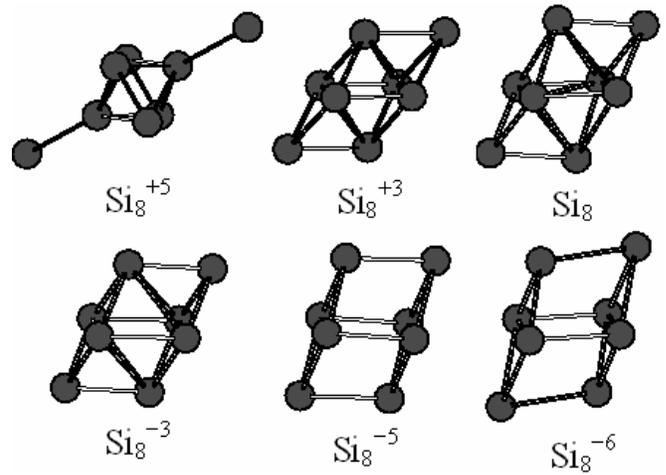


Figure 4 The stable structures of Si_8 cluster and its ions

Similarly, when five electrons are removed from Si_8 cluster, two atoms become adatom, which is somewhat similar to Si_7^{+4} cluster ion (see Fig.4). The negative Si_8 cluster structures still remain similar geometrical configuration to its neutral cluster.

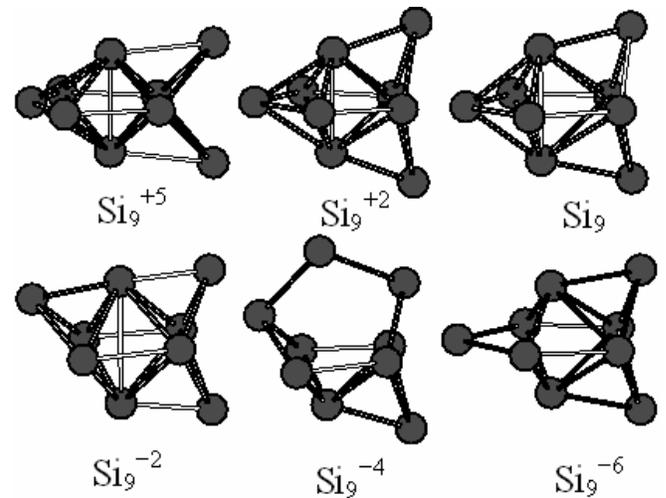


Figure 5 The stable structures of Si_9 cluster and its ions

Figure 5 presents the stable structures of Si_9 cluster and

its ions. According to figure 5, the positive ions still keep the bicapped pentagonal bipyramid structure. But the negative ions undergo significant structural distortion. Among the structures, the distortion in Si_9^{+4} ion is the most severe.

Si_{10} cluster is also an important because of its high stability like Si_6 cluster. Figure 6 shows its neutral and ionic structures. Similar to Si_6 cluster, the cationic and anionic structures of Si_{10} cluster keep its neutral geometrical configuration basically even though local distortion exists.

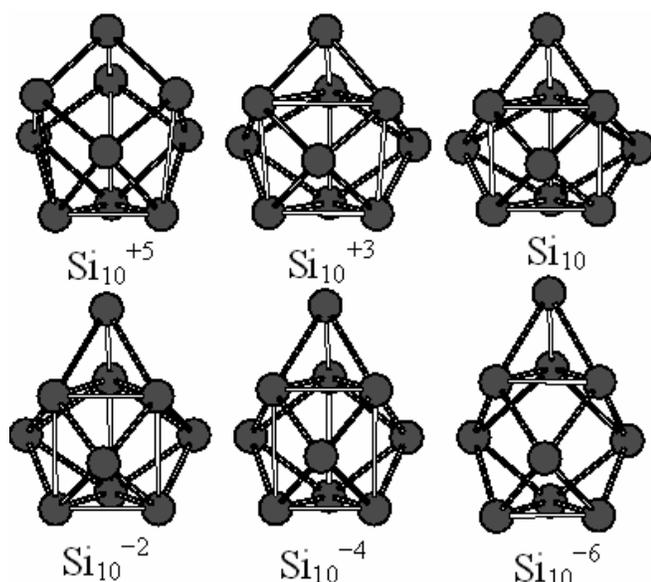


Figure 6 The stable structures of Si_{10} cluster and its ions

Cluster \ n	Si_n^{-6}	Si_n^{-5}	Si_n^{-4}	Si_n^{-3}	Si_n^{-2}	Si_n^{-1}	Si_n	Si_n^{+1}	Si_n^{+2}	Si_n^{+3}	Si_n^{+4}	Si_n^{+5}
5		1.69	1.02	1.18	2.87	2.50	2.08	1.77	0.97	1.66	0.40	
6	1.06	1.30	1.27	0.18	2.10	1.40	2.17	1.50	0.97	0.51	2.19	1.61
7	0.57	0.76	0.81	0.70	1.60	0.96	2.22	2.40	1.27	1.60	1.49	0.11
8	0.75	0.30	1.55	1.16	1.52	1.33	0.57	0.45	0.85	0.86	0.74	0.18
9		1.27	0.70	0.54	1.75	0.77	2.10	1.97	0.57	1.05	0.68	0.73
10	1.95	1.98	1.97	2.01	1.17	0.83	2.22	2.26	1.60	1.90	0.32	0.36

Table 2: Calculated energy gaps (E_g , in eV) between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO). Letter n is the atomic number of cluster.

The energy gaps (E_g , in eV) between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) for the neutral Si_n ($n=5-10$) clusters and their corresponding ions are presented in Table 2. Most of the energy gaps in Table 2 are larger than 1.0 eV. Our computational results show that the energy gaps for cationic Si_n^+ ($n=5-10$) clusters are closer to those of their corresponding neutral clusters. Our calculation shows

The electronic configuration of silicon atom is $3s^23p^2$. It usually adopt sp^3 hybrid. Therefore, Si atom hardly forms single or double bonds with other Si atoms in the clusters. Sometimes, even if there are the structures with single or double bonds, they are usually not very stable. When the electrons are removed from Si atom, its electronic configuration changes. The p electron in $3s^23p^1$ configuration forms single σ bond with neighbor atoms easily. The bonding characteristics in Si_7^{+4} , Si_7^{+5} and Si_8^{+5} ions probably belong to the situation. In addition, configuration $3s^23p^1$ can also produce edge atom with double bonds or planar structures by sp^1 or sp^2 hybrid. Si_5^{+4} and Si_7^{+5} ion structures probably arise from the bonding characteristics. On the other hand, the electrostatic repulsion between the positive atoms is another reason creating structural distortion. When the electrons are added into the clusters, new π bonds probably form between the atoms with additional electrons, which cause the increase of some bond strength. Of course, the negative atoms would be repulsed because of the electrostatic repulsion. The equilibrium bond lengths depend on the strength of the two forces.

that the ground state structures for neutral Si_n ($n=5-10$) clusters have a closed shell electronic structure with doubly occupied orbital. Removal of an electron from the highest doubly occupied orbital does not perturb the gap between HOMO and LUMO significantly. Therefore, for the closed shell electronic structures, the positive Si_n^+ ions would have about the same gaps as the neutral clusters. But because the additional electron in a negative Si_n^- ion goes into the lowest unoccupied

orbital, the gap is probably different from that of its corresponding neutral cluster. However, removal and adding of more electrons would result more and more severe structural distortion. The gaps change as charge increases or decreases. But, the correlation between the gaps and charge is not observed.

4 Conclusions

On charging the ground state structures of the small Si_n ($n=5-10$) clusters, they undergo structural distortion to some extent. The distortion depends on charge and their structures. The influence of charge on Si_6 and Si_{10} clusters is smaller relatively to other clusters. This indicates that the two clusters present high stability, which is in agreement with experimental results. The structural distortion results from the electrostatic repulsion among the charged atoms and the change of bonding characteristic. In addition, removal of charge causes the clusters to be unstable easily.

Acknowledgments

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